REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing this collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden to Department of Defense, Washington Headquarters Services, Directorate for Information Operations and Reports (0704-0188), 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302. Respondents should be aware that notwithstanding any other provision of law, no person shall be subject to any penalty for failing to comply with a collection of information if it does not display a currently valid OMB control number. **PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ADDRESS.**

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
2004	Conference Paper POSTPRINT	2001 - 2004

4. TITLE AND SUBTITLE
Substrate/oxide interface interaction in LaAlO$_3$/Si structures

5a. CONTRACT NUMBER
F29601-01-C-0241

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
62601F

6. AUTHOR(S)
T. Busani, R.A.B Devine

5d. PROJECT NUMBER
4846

5e. TASK NUMBER
RP

5f. WORK UNIT NUMBER
A1

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Air Force Research Laboratory
Space Vehicles Directorate
3550 Aberdeen Ave SE
Kirtland AFB, NM 87117-5776

8. PERFORMING ORGANIZATION REPORT NUMBER
AFRL-VS-PS-TP-2007-1014

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)

10. SPONSOR/MONITOR'S ACRONYM(S)
AFRL/VSSE

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited. (Clearance # VS03-0566)

13. SUPPLEMENTARY NOTES
Published in the Proc. Mat. Res. Soc. Symp **786** 189 (2004)

14. ABSTRACT
Amorphous lanthanum aluminate films (LaAlO$_3$) were deposited on Si substrates at room temperature using rf sputtering in pure Ar or an Ar/O$_2$ mixture with a stoichiometric target. The film composition was analyzed using XPS and EDX. The evolution of the material resulting from annealing at temperatures in excess of 900 °C was studied using infrared spectroscopy, XPS profiling and AFM. We obtain clear evidence for in-diffusion of Si from the substrate into the dielectric film. FTIR analysis showed only one peak centered at 747 cm^{-1} with an FWHM of 185cm^{-1} for as-deposited samples indicating an amorphous structure. Annealed samples showed very narrow absorptions at 483-510, 607, 695-720 and 811 cm^{-1}. No evidence for SiO$_2$ peaks at ~1060 cm^{-1} was observed suggesting that the LaAlO$_3$ structure tends not to reduce into a mixture of SiO$_2$ and a silicide. Short time annealing at 1000 °C results in a broad band at 905 cm^{-1} which can be interpreted in terms of the formation of a layer rich in Si-O-La bonds. Nitridation of the substrate before oxide deposition and annealing slows the degradation process but does not suppress it. X-ray diffraction analysis of the annealed films indicates a very oriented crystalline structure, yet unidentified, whose direction depends upon the orientation of the Si substrate. The dielectric constant in both annealed and as-deposited films was measured to be less than 14 and the leakage current density was very low. Some mobile charge was detected. This dielectric constant is substantially less than the value ~25 anticipated from bulk, single crystal measurements.

15. SUBJECT TERMS
LaAlO$_3$, Amorphous Films, Dielectric Film

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON: Capt John Boyd
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	Unlimited	7	**19b. TELEPHONE NUMBER** *(include area code)* 505-853-3157

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. 239.18

E6.12

Substrate/oxide interface interaction in LaAlO₃/Si structures

T. Busani[1] and R.A.B. Devine
AFRL-VSSE, Kirtland Air Force Base, Albuquerque, NM 87117
[1]also with Université Joseph Fourier, Grenoble, France

ABSTRACT

Amorphous lanthanum aluminate films ($LaAlO_3$) were deposited on Si substrates at room temperature using rf sputtering in pure Ar or an Ar/O_2 mixture with a stoichiometric target. The film composition was analyzed using XPS and EDX. The evolution of the material resulting from annealing at temperatures in excess of 900 °C was studied using infrared spectroscopy, XPS profiling and AFM. We obtain clear evidence for in-diffusion of Si from the substrate into the dielectric film. FTIR analysis showed only one peak centered at 747 cm^{-1} with an FWHM of 185 cm^{-1} for as-deposited samples indicating an amorphous structure. Annealed samples showed very narrow absorptions at 483-510, 607, 695-720 and 811 cm^{-1}. No evidence for SiO_2 peaks at ~1060 cm^{-1} was observed suggesting that the $LaAlO_3$ structure tends not to reduce into a mixture of SiO_2 and a silicide. Short time annealing at 1000 °C results in a broad band at 905 cm^{-1} which can be interpreted in terms of the formation of a layer rich in Si-O-La bonds. Nitridation of the substrate before oxide deposition and annealing slows the degradation process but does not suppress it. X-ray diffraction analysis of the annealed films indicates a very oriented crystalline structure, yet unidentified, whose direction depends upon the orientation of the Si substrate. The dielectric constant in both annealed and as-deposited films was measured to be less than 14 and the leakage current density was very low. Some mobile charge was detected. This dielectric constant is substantially less than the value ~ 25 anticipated from bulk, single crystal measurements.

INTRODUCTION

The dramatic expansion in technology and the communications market, including the one associated with high performance microprocessors as well as low-static power applications such as wireless systems [1], has driven industry to require greater integrated circuit functionality and performance at lower costs. This means an increase in circuit density for each Si wafer [2]. Obviously, device channel length and the SiO_2 gate dielectric thickness must decrease. However, SiO_2 layers thinner than ~ 1.3 nm have excessive leakage current (> 1 A/cm^2) simply due to direct tunneling through the oxide, and this is far too large for future circuits [3]. Unfortunately, the Semiconductor Industry Association road map indicates that a sub-1 nm effective oxide thickness (EOT) will be required for complementary metal-oxide-semiconductor (CMOS) devices with 50 nm gate widths so a dilemma exists.

An acknowledged solution (in principal) to the leakage current issue is to maintain the gate capacitance by increasing the dielectric constant (k) of the oxide and simultaneously thicken it. Though it is unlikely that the alternative oxide will have the excellent leakage properties of thermally grown SiO_2, a compromise may exist. Many materials acknowledged as "high-k", have been proposed in the last few years. They must satisfy a variety of criteria, such as thermodynamic stability in contact with the Si channel, potential barriers to both electron and hole injection from the substrate/inversion layer, low leakage, etc. Amongst the most commonly

studied materials were Al_2O_3, Ta_2O_5 and $SrTiO_3$, because they have a dielectric constant running from 9 to 80 and a band gap from 3.2 to 8.8 [4-5]. Interfacial reaction, resulting in the formation of SiO_2 or some low-k layer, has been observed in the case of Ta_2O_5 on Si [6] and in a Ta_2O_5 sandwich [7]. Furthermore, the barrier height to carrier injection is estimated to be rather small (< 0.5 eV). Al_2O_3 is potentially an attractive short term solution because of its relatively low dielectric constant (~ 9) but studies of Al_2O_3 deposited on Si(100) at temperatures below 400 °C [8] show evidence of an Aluminum silicate phase formed at the interface with Si. Because of this, an alternative gate dielectric needs to be found for a long-term industry solution.

$LaAlO_3$ has been investigated as an alternative dielectric since it is known that the La-O bonds in the metal oxide are strongly polarizable resulting in an increased dielectric constant. The crystalline phase of $LaAlO_3$ has k~ 28 and a band gap of 5.6 eV [5]. Many studies have demonstrated that it is possible to deposit $LaAlO_3$ layers of several nm onto Si with good electrical properties using different techniques [9-10]. The film is usually, however, amorphous. All these depositions were carried out at relatively high temperature (≥600 °C). Some of the films were recrystallized ex-situ.

In the present work we analyze in detail the effects of temperature on films deposited initially at room temperature. We demonstrate that it is not possible to obtain a desired crystalline phase for $LaAlO_3$ from this starting point.

## EXPERIMENTS

p- type Si(100) 3-5 ohm/cm resistivity wafers were first rinsed in pure HF acid then blown dry. Thin $(La_xAl_{1-x})_2O_3$ were deposited at room temperature by sputtering from a polycrystalline $LaAlO_3$ target using a 13.56 MHz radio frequency (rf) sputtering source (TORUS 2) with an Ar/O_2 gas mixture. The chamber pressure was 10 mTorr and the gas flow rates were set respectively at 75 sccm and 5 sccm. To optimise the stoichiometry of the deposited films the typical rf power was 60 W [9], calculations of the sputtering yield indicated that this power was appropriate for equal sputtering rates of the La and Al. Under these conditions $(La_xAl_{1-x})_2O_3$ films were obtained with x=0.6 as determined by x-ray photoelectron spectroscopy (XPS) profiling and electron microscopy spectroscopy (EDS) measurements.. The rate of deposition of the film was typically 1.4 nm/min, typical film thicknesses studied were ~ 100 nm. A second set of samples was prepared in the same conditions, but initially the Si surface was exposed to an N_2 plasma excited at 2.45 GHz . Such exposure is known to generate an ultra-thin Si_3N_4 layer, probably less than a mono-layer. The $(La_xAl_{1-x})_2O_3$ thickness and refractive index (n) for all films was determined using single wavelength (632.8 nm) ellipsometry, the thickness was confirmed by comparison of the Fourier Transform Infrared (FTIR) absorption and comparison with preceding work [9]. Surface analysis and roughness was carried out using an Autoprobe CP Atomic Force Microscopy (AFM) in a non-contact mode. The force used was 13.6 nN with a scanning speed of 3Hz. Capacitance-Voltage (C-V) curves were measured at 100 KHz using a Keithley 590 system after deposition of Al dots of 0.0078 cm^2 on the dielectric surface. The back face of the wafer was metallized to ensure good electrical contact. Prior to electrode deposition the wafers were cleaved and some samples were subjected to rapid thermal annealing between 900 to 1000 °C for 1 to 5 min. in N_2 or N_2H_2 atmospheres in an attempt to minimize La and Al interactions with the silicon substrate. Finally X-ray diffraction intensity data was obtained in a 0.02° step interval in the 2θ range between 10 and 80° with a measurement time of 1.2 sec. A Cuα1 source was used.

RESULTS AND DISCUSSION

LaAlO₃ has a ideal perovskite cubic structure Pn3m which presents three dominant IR active modes: v_1 corresponds to stretching of O atoms along the Al-O-Al line, v_2 is perpendicular to this line, and v_3 is the La translation respect to Al and O atoms. This crystal is typically presented as a rhombahedral deformation with two arrangements for the fundamental cell (space group R3m). The octahedral AlO₆ are quite regular with an Al-O length of 0.190 nm, the bond length of La-O is ~0.25 nm [11]. We observe that the bond force constants for La-O and La-Al are weak compared to Al-O in the AlO₆ octahedra. This helps us to separate the vibrational modes into *internal*, when we considered the movements of Al or O in the AlO₆ cell, and *external*, related to the La movement respect to AlO₆ octahedra. Since the crystal symmetry is lower, some IR inactive modes become active and new vibrations may appear in the spectra. An example is the v_1 vibration which is predicted to be split into two peaks depending upon crystal deformation. Saine et al. [11] give the relation of the AlO₆ modes among cubic, rhombahedral and isolated structures.

In Figure 1a we show typical absorbance IR spectra of the room temperature deposited films.
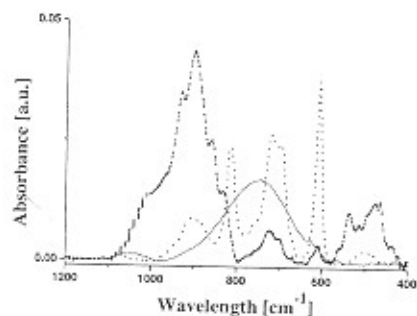
Figure 1a. Normal incidence absorbance IR spectra of $(La_xAl_{1-x})_2O_3$ deposited on a Si wafer. The solid line refers to as-deposited oxide, the dotted line is after annealing at 950 °C in an N₂ atmosphere for 1 min. and the square dashed line is after annealing at 1000 °C for 1 min.
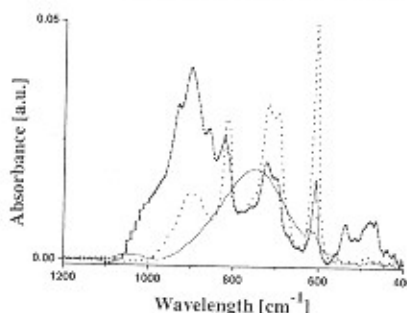
Figure 1b. Normal incidence absorbance IR spectra of $(La_xAl_{1-x})_2O_3$ deposited on a previously nitrided Si wafer. The solid line refers to as-deposited oxide, the dotted line is for the sample after annealing at 950 °C in N₂ atmosphere for 1 min. and the square dashed line is for a sample annealed at 1000 °C for 1 min.

The solid line is representative of the as-deposited oxide and shows one intense peak at 747 cm⁻¹ and a very small peak around 1050 cm⁻¹ The latter is due to the formation of an initial SiO₂ layer during ignition of the Ar and O₂ plasma. The evidence of an amorphous structure is confirmed by the full width at half maximum (FWHM) of 185 cm⁻¹ of the main peak. One can very crudely approximate:

$$v = \frac{1}{\lambda} = \frac{1}{2\pi c}\sqrt{\frac{f}{\mu}} \qquad (1)$$

where v is the vibration mode frequency in a B-O molecule (B being Al or La) expressed in cm^{-1}, $\mu=(m_B m_O)/(m_B+m_O)$ is the reduced mass, m_O and m_B are the atomic weight in Kg of cation B and anion O, $f=17/r^3$ is the stretching force constant and r is the B-O length. We can estimate the theoretical frequency in the pure, binary glasses B_2O_3 using the bond lengths for La-O and Al-O [12-13]. We find that the stretching modes are respectively at 355 and 778 cm^{-1}. From eq. (1), the wave number of the vibration is inversely proportional to the value of the reduced mass. In consequence, we can conclude that the presence of La in LaAlO$_3$ glass probably has the effect of moving the IR spectra to lower frequencies than that for pure Al$_2$O$_3$ which is consistent with the result for the amorphous phase shown in Figure 1a.

The dotted line in Figure 1a shows a typical IR absorbance spectra for a sample annealed at 950 °C for 1 min. We observe similar spectra in samples where the anneal was carried out at 950 °C for 15 min and 950 °C for 4 min, in an N$_2$ or N$_2$H$_2$ atmosphere. First we note that the intensity of SiO$_2$ small peak does not increase, suggesting that little or no oxygen from the (La$_x$Al$_{1-x}$)$_2$O$_3$ diffuses and reacts at the Si substrate interface. There are 4 very narrow peaks at 483-510, 607, 695-720 and 811 cm^{-1} indicating a polycrystalline or local crystalline structure. The 695-720 cm^{-1} peak is the v_1 vibration of the octahedral AlO$_6$ and the mode at 510-483 cm^{-1} could be attributed to v_2 mode. According to Saine [11] in the rhombahedral structure we should see another peak at 565 cm^{-1} related to the v_1 mode in a cubic cell while a peak at 511 cm^{-1} is related to the angular deformation of O-Al-O due to phase movements between two octahedra. This vibration is impossible in the AlO$_6$ isolated structure. Abrashev et al. [15] have calculated the transverse optic/longitudinal optic (TO/LO = 481/505 cm^{-1}) peak positions for the v_2 mode. Normally, we do not expect to observe LO peaks, since our IR spectra were measured at normal incidence. However, as shown in Table I, our annealed samples have a significant roughness of several tens of nm, which suggests that the IR beam does not see a flat surface and with such roughness the beam incidence will be non-normal for parts of the surface. Under these conditions the Berreman effect [16] will be active and the LO mode may be excited. Unfortunately v_3 is too low in wave number to be visible by our instrument and this does not help to confirm the presence of LaAlO$_3$ crystal structure.

Sample description	Max height between adjacent peaks [nm]	Average roughness [nm]
(La$_x$Al$_{1-x}$)$_2$O$_3$ as-deposited / Si substrate	2.25 / 2	<1
(La$_x$Al$_{1-x}$)$_2$O$_3$ ann 950 °C 1 min / Si substrate	60-70 / 60	18.18
(La$_x$Al$_{1-x}$)$_2$O$_3$ +Si$_3$N$_4$ ann 950 °C 1 min / Si substrate	37 / 3.6	11.27

Table I. AFM surface analysis data for different samples. The words "Si substrate" indicate the AFM is carried out on the Si after the oxide layer has been removed.

There are other arguments to suggest that these peaks are not related to a LaAlO$_3$ single phase. If one plots the intensity of the peaks as a function of film thickness, the resultant curve does not go through zero, which it should if one deals with peaks emanating from the same vibration. The XRD data presented in Figure 2 demonstrates that the oxide is in a crystalline phase, but that it is not that of idealized LaAlO$_3$.

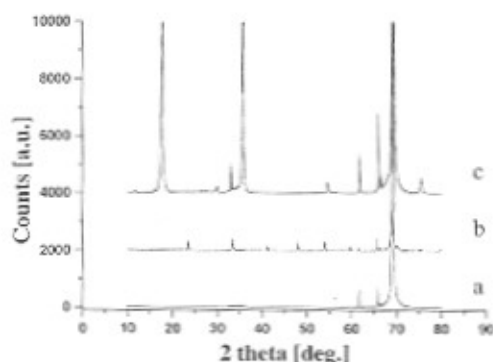**Figure 2**. XRD of

a) Si (100) substrate,

b) LaAlO₃ polycrystalline powder on Si (100) and

c) $(La_xAl_{1-x})_2O_3$ deposited on Si and annealed at 950 °C for 1 min.

We also identify a broad peak at ~900 cm⁻¹ that is the beginning of the interfacial reaction between Si and La. This interaction has been reported [14] as a vibration of the RE-O-Si bond (RE = rare-earth) in different oxides. It is evident that increasing the annealing temperature to 1000 °C, even if for 1 min, results in this peak becoming predominant and the others decrease considerably. The peak at 808 cm⁻¹ is less intense, even if still important, and we identify this with the presence of an alumino-silicate structure [17]. We can conclude that Si starts to form more La-O-Si but also Si-Al-La bonds containing oxygens. We have tried to eliminate this effect using an Si₃N₄ protecting layer as described previously, the results are shown in Figure 1b. When compared with Figure 1a, it appears that the silicon nitride layer does not suppress the annealing phenomenon, but it does tend to limit it.

The AFM (Table I) and XPS (Figure 3) data further help in the understanding of interfacial degradation and reaction in the $(La_xAl_{1-x})_2O_3$ /Si system. The measurements were carried out first on the annealed and unannealed samples then the oxide was removed and Si surfaces were analysed. The roughness of the oxide surface is really significant in all samples that
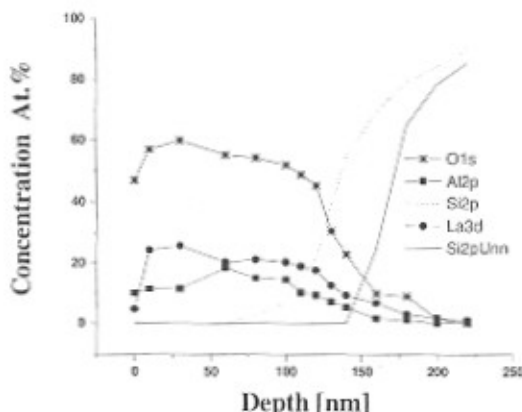

Figure 3. XPS data of $(La_xAl_{1-x})_2O_3$ deposited on Si and annealed at 950 °C for 1 min. The profile for "Si2pUnn" refers to as-deposited samples. The Si signal appears before the Si substrate is encountered. For the amorphous (as-deposited) case(solid line), there is no evidence for Si in the oxide layer.

received a thermal treatment, but less important on that where Si_3N_4 layer was grown prior to deposition. These observations are interpreted as indicating that Si diffused in the oxide layer during the high temperature anneals leaving a "roughened" structure. The XPS profile data is shown in Figure 3. Though there is always some imprecision in XPS about the exact location of the dielectric/Si interface, we clearly evidence that in an annealed sample, Si appears to be present well into the region we call the "dielectric". In fact, an anneal at 950 °C for 1 minute appears to suffice for Si to penetrate ~ 40 nm. Note that this exceeds by a factor ~ 2 the average roughness of this sample so the Si signal does not arise from the substrate, only from the film. All of these observations are consistent with the appearance of an La-O-Si associated vibrational mode in the infrared absorption spectrum as a direct result of annealing.

Finally, C(V) and current density electric field (I-V) measurements were carried out to test the electrical quality of the interface and the oxide. For the amorphous, as-deposited films we find k lower than 14 and the leakage current density ~ 10^{-8} A/cm^2 for an electric field ~ - 1 MV cm^{-1}. These results are consistent with earlier findings [9]. A hysteresis effect is also visible and this does not reduce when moderated annealing, say 400 °C for 30 min in a inert atmosphere, is employed even though the flat band voltage moves from −10 V to -1.5 V.

In the light of these experiments, we are not surprised that is hard to obtain a high k oxide. The crystal phase of $LaAlO_3$ fails to appear before significant interaction with the underlying Si has occurred. In order to employ $LaAlO_3$ in a high k application (k ~ 25) it is necessary to find a means of depositing densified or crystallized material and to avoid significant post-deposition annealing at high temperatures.

REFERENCES

1. http://public.itrs.net
2. G. Baccarani, M.R. Wordeman, and R.H. Dennard, IEEE Trans. Electron Devices **31**, 452 (1984)
3. S.M. Lo, D.A. Buchanan, Y. Taur, and W. Wang, IEEE Electr. Dev. Lett. **18**, 209 (1997)
4. G.D. Wilk, R.M. Wallace, J.M. Antony, J. Appl. Phys. **89**, 5243 (2001)
5. P.W. Peacock and J. Roberts, J. Appl. Phys. **92**, 4712 (2002)
6. G.B. Alers, D.J. Werder, Y. Chabal, H.C. Lu, E.P. Gusev, E. Garfunkel, T. Gustafsson, and R. S. Urdhal, Appl. Phys. Lett. **73**, 1517 (1998)
7. P.K. Roy and I.C. Kizilyalli, Appl. Phys. Lett. **72**, 2835 (1998).
8. T.M. Klein, D. Niu, W.S. Epling, W. Li, D.M. Maher, C.C. Hobbs, R.I. Hedge, I.J.R. Baumvol, and G.N. Parsons, Appl. Phys. Lett. **75**, 4001 (1999)
9. R. A. B. Devine, J. Appl. Phys. **93**, 9938 (2003)
10. Byung-Eun Park, H. Ishiwara, Appl. Phys. Lett. **82**, 1197 (2003)
11. M.C. Saine, E. Husson, and H. Brusset, Spectrochimica Acta **73A**, 985 (1981)
12. E.F. Archibong, and A. St-Amant, J. Phys. Chem. A **103**, 1109 (1999)
13. R. El-Mallawany, A. Abdel-Kader, M. El-Hawary, and N. El-Khoshkhany, Eur. Phys. J. AP **19**, 165 (2002)
14. H. Ono, Appl. Phys. Lett. **78**, 1832 (2001)
15. Abrashev, M.V., Litvinchuk, A.P., Iliev, M.N., Meng, R.L., Popov, V.N., Ivanov, V.G., Chakalov, R.A.; Thomsen, C., Phys. Rev. B **59**, 4146 (1999)
16. D.W. Berreman, Phys. Rev. **130**, 2193 (1963)
17. W. Mozgawa, and M. Sitarz, J. Mol. Struc. **614**, 273 (2002)